EXAFS Studies of Non-Heme Iron Enzymes and Copper Chaperone Protein Atox1

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Abstract No. que9159
Beamline(s): **X9B**

X-ray absorption spectroscopy has been very useful for characterizing the structures of metalloenzymes, their reaction intermediates, and metastable inorganic species that serve as models thereof. In the past year at NSLS, we have obtained EXAFS data on (a) a peroxo intermediate of a fatty acid Δ^9-desaturase and its decayed form, (b) a peroxo intermediate at the initial stage of ferritin core assembly in *E. coli*, (c) synthetic high valent iron-oxo and iron-peroxo complexes relevant to the oxygen activation mechanism of the nonheme iron enzymes, and (d) copper bound to the Cu-transporting ATPase associated with Wilson disease and the human copper chaperone protein Atox1.

Our preliminary XAS data analysis show that there is a significant difference in the diiron core structures of the peroxo intermediate of Δ^9-desaturase and its decayed form. Specifically, the Fe-Fe distance in the peroxo intermediate is much longer than that found in the decayed form. Furthermore the XAS spectrum of the Δ^9-desaturase peroxo intermediate is quite different from that of the ferritin peroxo intermediate, despite the fat that the two intermediates have similar Mössbauer and Raman spectra. Preliminary analysis of the *E. coli* ferritin peroxo intermediate shows a short Fe-Fe distance (2.5 Å) similar to that reported for the frog ferritin peroxo intermediate. Our study of the Wilson disease ATPase shows that copper(I) is bound to two cysteines with an S-Cu-S angle of less than 180 degrees; this study has been completed and is now published. Our preliminary analysis of Cu-bound Atox1 shows that it does not bind to methionine residue and its XANES spectrum is unlike that of the corresponding yeast Atx1 protein.